



how fast, in what order, and over what barrier

Rate, and the words that are not synonyms

- **average rate** is the change in concentration over a finite interval; **instantaneous rate** is the limit as that interval shrinks, read as the slope of the tangent
- for $aA + bB \rightarrow cC + dD$ the single rate is $-(1/a)d[A]/dt = -(1/b)d[B]/dt = +(1/c)d[C]/dt$, so every species gives the same number once divided by its coefficient
- a reactant term carries a MINUS sign because its concentration falls, and quoting a rate as negative is a sign error not a result
- units of rate are mol per litre per second, whatever the order; the units of the rate CONSTANT are what change with order

Rate law and order, which the equation cannot tell you

- the **rate law** is found by EXPERIMENT: $\text{rate} = k[A]^x[B]^y$, and x and y have nothing to do with the balanced coefficients unless the step really is elementary
- **order** is $x + y$, the sum of the exponents; it can be zero, fractional or negative, because it is a measured quantity
- **molecularity** is the number of species colliding in ONE elementary step, so it is a whole number, at least 1, and never applies to an overall reaction
- for a multi step reaction the **slowest step is rate determining**, and the observed order comes from that step alone, which is why order and coefficients disagree

Order, and the units that give it away *

Order	Rate law	Units of k
zero	$\text{rate} = k$	mol per litre per second
first	$\text{rate} = k[A]$	per second
second	$\text{rate} = k[A]^2$	litre per mol per second
n th	$\text{rate} = k[A]^n$	$(\text{mol per litre})^{1-n}$ per second

if a question gives you the units of k and asks for the order, this table is the whole answer

The integrated rate laws

zero order

$$[A] = [A]_0 - kt$$

zero order half life

$$t_{1/2} = [A]_0 / 2k, \text{ so it DEPENDS on the starting amount}$$

first order

$$k = (2.303/t) \log ([A]_0 / [A])$$

first order half life

$$t_{1/2} = 0.693 / k, \text{ independent of the starting amount}$$

first order, straight line form

$$\log [A] \text{ against } t \text{ is a straight line of slope } -k/2.303$$

a constant half life is the signature of first order, and it is the quickest test a question can ask you to apply

